Concentration and oxidative potential of on-road particle emissions and their relationship with traffic composition in a long road tunnel

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Abstract

The relationship between the physical properties and oxidative potential of vehicle particle emissions and traffic composition was investigated in a 4.5 km road tunnel in Brisbane, Australia. Particle number, particle mass ($PM_{2.5}$), CO, CO_2 and particle associated reactive oxygen species (ROS) were measured using mobile sampling. The profile of particle number and $PM_{2.5}$ concentration with distance through the tunnel was determined, and demonstrated marked relationships between particle concentration and both road gradient and tunnel ventilation. ROS levels in the tunnel were found to be high compared to an open road with similar traffic characteristics, which was attributed to the substantial difference in estimated dilution ratios. Principal component analysis (PCA) revealed that the levels of pollutants were generally better correlated with total traffic count, rather than the traffic composition. PCA also showed that the ROS levels in the tunnel were well correlated with particle mass and CO concentrations. These findings contribute towards better understanding the characteristics of particles encountered by vehicle occupants and potential associated health effects.

1.0 Introduction

Many studies have demonstrated detrimental health effects due to airborne particles, especially those in the ultrafine size range (D_p < 100 nm, UFP) [1-4]. In urban environments, vehicle emissions are the major source of UFP [5]. The toxicity of vehicle particulate emissions is thought to be related to both their chemical composition and size [3, 6]. The chemical composition of UFP can cause cellular damage via oxidative stress [4]. Therefore, characterizing and quantifying vehicle particulate emissions and their chemical composition under real world conditions are necessary to better appreciate their potential health effects.

An indication of particle toxicity can be obtained by measurement of particle associated reactive oxygen species (ROS). Particles that include or can generate ROS have been shown to elicit adverse health effects through their ability to cause oxidative stress [1, 4, 7]. Particle associated ROS have been detected in diesel and gasoline emissions [8, 9], however, a more comprehensive understanding of vehicle emissions of particle associated ROS, and their relationship with road and traffic parameters under real world (as opposed to dynamometer) conditions is lacking.

Road tunnels are ideal locations in which to measure vehicle emissions, as the influence of meteorological conditions is minimized. On road UFP concentrations are highly dynamic, and on-road measurements can capture the characteristics of those entering vehicle cabins [10]. Road tunnels

can be an especially high exposure environment [11, 12]. On road measurements can also provide information on the influence of roadway factors, such as gradient, on vehicle emissions [10, 13-15]. While there have been several studies that have shown that the road gradient in a tunnel can affect the concentrations of gaseous pollutants [13-15], there have only been limited on road measurements of the effects on vehicle particle emissions [10]. As such, the understanding of tunnel roadway characteristics on vehicle particle emissions is incomplete.

This study aimed to contribute towards addressing the knowledge gaps outlined above by quantifying the effect of tunnel characteristics, namely gradient and ventilation, on vehicle emissions. In addition, we aimed to assess the oxidative potential of particles present in the tunnel under real world conditions. Through this, we sought to better understand the characteristics of particles to which car occupants are exposure as they relate to potential health effects. Finally, we aimed to determine the effects of traffic number and composition on the concentration of particle number, particle mass and particle associated ROS in the tunnel were also considered in order to develop a location-specific model relating these variables that could assist existing monitoring and management practices.

2.0 Methods

2.1 Setting

Measurements were conducted in a recently opened (March 2010) road tunnel in Brisbane, Australia. The tunnel runs in a north-south direction and consists of two unidirectional bores each with two lanes, is 4.5 km long, with a maximum speed of 80 kmh^{-1}. The tunnel is currently Australia's longest. There are two northbound entries to the tunnel, one of which is 1.5 km along the tunnel, and a single exit at the northern end. The southbound bore has one entry and two exits, with one exit 3 km along the tunnel. The gradient of the tunnel from the northbound entry is a downhill slope of 5% for 0.5 km followed by a near flat section for 1 km until the second entry point whereby it slopes downhill at 3.5% for 1.5 km and finally uphill for 1.5 km at 3.5%. The opposite applies in the southbound bore. The tunnel has a longitudinal ventilation system and there are no portal emissions permitted. The difference between the bores is the location of the main air extraction point. In the southbound bore air is extracted 0.5 km from the exit, while for the northbound section the main extraction point is located immediately adjacent to the exit.

2.2 Instrumentation

A TSI 3007 condensation particle counter (CPC) was used to measure particle number from 10 to >1000 nm every second, although the great majority of particles are expected to fall in the UFP size range [5]. The 3007 can detect a maximum concentration of 10^5 particles cm^{-3} before coincidence error becomes significant [16]. Accordingly, we developed a correction factor based on contemporaneous measurements with a TSI 3022A CPC, found in the supporting information. The exponential correction factor we used was very similar to that calculated by Westerdahl et al. [17] based on an analogous approach, and was applied to all data points greater than 10^5 particles cm^{-3}.

A TSI 8520 DustTrak was fitted with a 2.5 µm impactor and measured $PM_{2.5}$ concentration every second. The DustTrak is an optical instrument, and its calibration is based on an aerosol different to that encountered on-road. As such, a correction factor was used that was based on simultaneous measurements with a tapered element oscillating microbalance (TEOM) in a Brisbane tunnel as reported by Jamriska et al [18]. A TSI IAQ-Calc 7545 gas analyser was used to measure concentrations of CO and CO_2 in addition to temperature and relative humidity.

A new profluorescent nitroxide probe, BPEAnit**,** was used for the detection of particle based ROS as described in Miljevic et al. [19]. To ensure enough particle mass was sampled for the BPEAnit assay, the probe sampled cumulatively for the 4 or 6 tunnel journeys that comprised a sampling trip and this constituted one ROS sample. The pump used for BPEAnit assay started operating at the entrance to the tunnel and was stopped at the exit so that only tunnel air was sampled. The assay result was calculated for each sampling trip and normalised to the particulate matter mass, which was calculated by integrating corrected DustTrak readings over the sampling period. These values presented oxidative potential of particles, hereafter referred to as ROS concentrations.

2.3 Sampling Approach

The CPC and DustTrak were set up inside a vehicle and connected to a common sampling point located on the outside of the vehicle and facing the direction of travel. A 0.8 m conductive rubber tube was used to minimise particle diffusion losses in the UFP range. The Q-Trak probe was attached to the outside of the vehicle near the tubing inlet. The sampling inlet leading to the impingers with the BPEAnit solution sampled from the rear driver side facing the direction of travel. The research vehicle used unleaded petrol and was in excellent condition. A video of each tunnel run from the vehicle's dashboard was taken to record the traffic conditions and events encountered.

Measurements were conducted over three sampling campaigns in March (I), July (II) and August/September (III), 2010. ROS measurements were conducted during campaign III only. On each sampling day the there were 2-3 sampling exercises that comprised 2-3 trips through each bore. The sampling times ranged from 07:00h to 20:00h in order to encounter a range of different traffic conditions. A total of 182 trips were performed, with 50 in campaign I, 60 in II and 72 in III, and these were evenly distributed across the two bores.

All instruments were run continuously throughout leaving the Queensland University of Technology campus, performing tunnel measurements, and returning to the university. This permitted collection of additional open road data en-route to the tunnel. The same route was taken from the university to the tunnel and for the return journey, and it comprised travel on two major roads (Riverside Expressway and Innercity Bypass) with higher traffic volumes, 135,000 and 70,000 vehicles per day [20], than those in the tunnel.

Traffic count and composition data for the tunnel were supplied at hourly resolution by its operators, Rivercity Motorways. Vehicles were classified into 3 categories; short vehicles referred to those vehicles less than 7 m, medium vehicles defined as those between 7 and 12 m, while long vehicles were classified as being over 12 m. The sum of the medium and long vehicles was assumed all diesel vehicles and classed as heavy diesel vehicles (HDV) in our analyses.

Open road measurements were performed in October 2010 on a road with analogous traffic counts, composition and speed limit to the tunnel. This was done to enable comparison of ROS concentrations under different dilution conditions to those in the tunnel. Particle number and mass measurements were also taken. The sampling times for the BPEAnit assay were between 16 and 24 minutes to mimic the total sampling times of 4-6 tunnel trips.

2.4 Data analysis

For both bores, the tunnel runs were classified as to whether HDV were encountered by visual observation during the run to determine their impact on the measured parameters. A model of the

particle number and mass concentration evolution through the tunnel for the northbound and southbound bores was constructed for each of these scenarios to identify the effect of traffic and tunnel characteristics. In the tunnel, there are four main roadway sections each with a different gradient. Each tunnel run was therefore divided into four corresponding sections. The slope of particle concentration profiles over distance traversed in each section was calculated. The median of the slopes calculated for all the runs was used to represent a typical profile. The 25^{th} and 75^{th} quartile were also calculated to indicate the spread of data. Dilution ratios corresponding to ROS measurements performed during campaign III were calculated according to the method described in Ntziachristos et al. [21] (Supporting information). Principal component analysis (PCA) was applied to the campaign III data to identify any correlations between ROS, pollutant levels and traffic data.

3.0 Results and Discussion

3.1 Overall results

The average total vehicle counts per bore in the tunnel during campaigns I, II and III were 1728, 1029 and 1112 vehicles h^{-1}, respectively. The decrease in count is attributed to the introduction of a toll after campaign I. The traffic composition was similar between the three campaigns, with short vehicles representing 79, 77 and 74.3%, medium vehicles representing 15.6, 17 and 19.6% and long vehicles constituting 5.4, 6.3 and 6.1% of the total traffic on average, respectively. The average time taken to travel through the northbound bore was 3 min 56 s, while for the southbound bore it was 4 min 4 s. The average concentrations measured during each campaign are given in Table 1. No CO data was collected during campaign II due to instrument error.

Table 1

3.2 Profile of particle number and mass concentration over distance through the tunnel

The concentration profiles of particle number based on all southbound and northbound runs are shown in Figures 2 and 3, respectively. Particle mass profiles are shown in Figures 4 and 5, respectively. These all show differences between the two bores correlates with ascending and descending sections in the two bores. The southbound bore exhibits a pattern characterised by an increase upon entering the tunnel, with a sharper increase on the first ascending section followed by the concentration levelling out on the relatively flat section. This sharper increase is attributed to greater vehicle engine load and associated increase in emissions. However, in the last section there is a decrease in concentration that is attributed to the tunnel ventilation system, as the main extraction point is located at the start of this section. For the last section of the southbound bore the 25^{th} quartile values became negative, this was due to the large variation observed in particle number and mass concentrations.

In contrast, data from the northbound bore exhibits increasing concentrations throughout the entire bore, with the largest increase on the ascending section and smallest on the descending section. This has been observed before in the concentration of particle number [10] and particle mass [14]. The ventilation system at the northbound exit is sited almost at the terminal end of the bore, and its effect on the concentration is subsequently much less marked than in the southbound bore. This indicates that the location of the ventilation system had a significant effect on the pollutant levels irrespective of the gradient in this tunnel. The concentration of particle number and mass in the tunnel was observed to be related to the gradient in the tunnel, with a sharper increase found on the uphill sections compared to the flat and downhill sections. This implies that the gradient of the road can be used as a predictor for the rate of change in concentration of particle number and mass. This is

particularly true in this tunnel as traffic speeds were relatively consistent across the sampling runs, due to the tunnel travel times all being very similar for each trip and so removed the effects of different engine cycles.

The profiles for the tunnel trips that were classified according to the immediate presence of HDVs; these are presented in the supporting information. The profiles showed similar variation in the concentration for the particle number and mass profiles when compared to those collected in the absence of HDVs. While we were able to identify HDV in the immediate vicinity of our research vehicle, there may have been influence from HDVs that were outside our view.

Although there was little difference observed between the classified trips in the variation in concentration, there were some differences in the concentration medians from one classification to another. The median particle number concentration in the first section of the southbound bore was approximately 20% higher when HDV were observed in the tunnel. The median southbound particle mass concentrations were similar for both classifications. There were no differences observed in the northbound bore for median concentrations. Overall, there was a poor relationship between HDV levels and particle number and mass concentrations based on their effect on tunnel concentration profiles.

The lack of readily discernible influence of HDVs is in contrast to previous studies in road tunnels, where they exerted considerable influence on particle number and mass concentrations [11, 22, 23]. Using a similar mobile sampling approach to the present study, Knibbs et al. [11] found that hourly HDV traffic volume was a fair to very good determinant of UFP concentration in the two bores of a road tunnel in Sydney, Australia. Stationary sampling was employed at the Caldecott tunnel, San Francisco and a clear increase in particle number concentration as a result of a small increase in the percentage of diesel vehicles was observed [22, 23]. Although there is a large percentage of HDV (23%) in the tunnel in our study, and certainly much higher than in the studies by Geller at al. [22] (3.8%) and Knibbs et al. [11] (7%), the absolute number of HDV encountered in our tunnel were quite low as during the sampling we observed a maximum of only a few HDV per tunnel trip, and sometimes less. Their contribution appears to be largely indistinguishable from the contribution of the overall vehicle, which was predominantly comprised of gasoline vehicles. Mobile sampling is more heavily influenced by the number and type of vehicles in the immediate vicinity of the sampling vehicle compared to stationary sampling, and this could partially explain why the presence of HDV was a poor determinant of higher concentrations in this study.

Figure 1-4

3.3 Oxidative potential of particle emissions

Particle associated ROS were detected in all but one of the sampling trips in the tunnel, and concentrations ranged from 0 - 1182 nmol mg^{-1} of particle mass, as shown in Table 2. During open road measurements there were no detectable levels of ROS associated with the particles sampled. Therefore, the ROS particle concentrations in the tunnel were elevated compared to an open road with similar traffic characteristics. On the 1/9/2010, the concentration of all three ROS samples collected on that day were 225, 759, 1182 nmol mg^{-1} compared to the average of the other sampling days of 206 nmol mg^{-1}. The higher than average levels on that day were attributable to controlled vegetation fires in the local area on that morning; wood smoke was previously found to have high ROS content [24]. The particle number concentrations outside the tunnel on the open road were found to be more than

twice that inside the tunnel during the morning sampling, further highlighting the contribution of vegetation fires to the overall particle number. The particle mass was noticeably higher both outside and in the tunnel compared to other sampling days.

Table 2

The ROS levels detected in the tunnel in this study are high compared to other studies [8, 25]. A recent dynamometer study using the same BPEAnit assay [8] found in diesel exhaust the concentration of ROS was 50 nmol mg^{-1} at 100% load at 1700 rpm, which is substantially lower than ROS levels observed in the tunnel. Although dynamometer studies involve emission characteristics of an individual engine under controlled driving conditions and therefore cannot be directly compared with on-road studies, this still suggests that diesel exhaust might not be the predominant source of increased BPEAnit fluorescence upon sampling PM emissions in this tunnel study.

The dithiothretiol (DTT) method, has also been used to measure oxidative potential of particulate matter [25]. Though the DTT assay results are not directly comparable with those from a BPEAnit probe, relative trends can be compared. In the 1.1 km Caldecott tunnel, the highest DTT activity per particle mass was found in the gasoline vehicles only bore [25]. This result is in agreement with other dynamometer studies that used the DTT assay [9, 26] which found higher ROS activity per mass of particles emitted by gasoline vehicles compared to diesel vehicles. In addition, the oxidative potential of diesel exhaust particulate matter strongly depends on the presence and type of after treatment device being used [27]. Considering the results of these studies and taking into account that the majority of vehicles passing through this tunnel are light-duty vehicles (see Table 2), it would appear that gasoline vehicles are primarily responsible for the oxidative potential of the particulate matter emissions in the tunnel we investigated. This finding has implications for assessment of health risk assessment near roadways, as previous studies [11, 28] have shown HDV volume to be a strong determinant of on-road UFP concentrations. If, however, it is gasoline vehicles that are primarily responsible for oxidative capacity of particles, then both modelling and measurement of on- and near-road exposures should reflect this.

In contrast to the tunnel, sampling on an open road with similar traffic characteristics did not result in increased BPEAnit probe fluorescence. Therefore, the ROS levels and associated oxidative potential of these PM emissions were below detectable levels. This is potentially attributable to different dilution ratios in the two sampling environments, with tunnels characterized by low dilution rations (Table 2) when compared with the unconstrained dilution possible on open air roadways [27]. The gas to particle partitioning of semi-volatile (organic) compounds, which have been found to contribute to oxidative potential of PM emissions [24, 27] strongly depends on dilution conditions, with lower dilution conditions leading to a higher fraction of semivolatile compounds in the particle phase. Biswas et al [27] have reported that PM oxidative potential as measured by the DTT assay increases as the dilution ratio increases. Unlike this, a strong correlation was not found between dilution ratios and ROS levels in this tunnel study [27]. This could be due to the small range of dilution ratios measured in this study (500 – 1000). Another reason could be due to the method of sampling as in this study a mobile platform was utilised as opposed to a fixed sample point. The fixed sampling point is better suited for the calculation of average emissions, whereas mobile platform can be caught in a plume behind a certain vehicle. However, mobile sampling is more representative of the characteristics of particles to which commuters are exposed.

3.4 Principal Component Analysis

The PCA loadings plot is given in Figure 6. It shows that that, in general, the levels of pollutants were better correlated with total vehicle count than traffic composition. In particular, the concentration of particle associated ROS was better correlated with the total traffic count, as well as mass and CO concentration. The traffic composition was not related to the ROS levels in the tunnel, and had little correlation with other pollutants. Particle number and mass concentrations exhibited little variance in the loadings plot, which demonstrates that HDV had little influence on pollutant levels, and this is possibly due to the low absolute numbers encountered in the tunnel. What was observed in the concentration profiles is in agreement with the loadings plot. That is, total vehicle count was a better indicator than traffic composition of the pollutant levels in the tunnel. The PCA has also shown that the ROS levels and the concentration of other pollutants were more correlated with the traffic volume than traffic composition. This is in contrast with other mobile sampling studies [28] where the concentration of the measured pollutants was related to the traffic composition, specifically the HDV volume. However, due to the traffic through the tunnel predominantly being gasoline powered, the association between ROS levels and traffic volume we observed is in agreement with other studies [9, 26], which also found that gasoline vehicles had higher ROS activity per mass of particles emitted. This has implications for commuter and near-road particle exposure, as gasoline vehicles often make up the large majority of urban vehicle fleets, and their emissions can be characterized by increased ROS which is potentially associated with greater particle toxicity. Although HDV volume is often well-correlated with UFP concentrations, if the trends observed in this and other recent studies are further validated by future work, then it should signal the need to consider gasoline vehicle volume as a key parameter when evaluating potential ultrafine and fine particle health effects on and near roadways.

Figure 6

References

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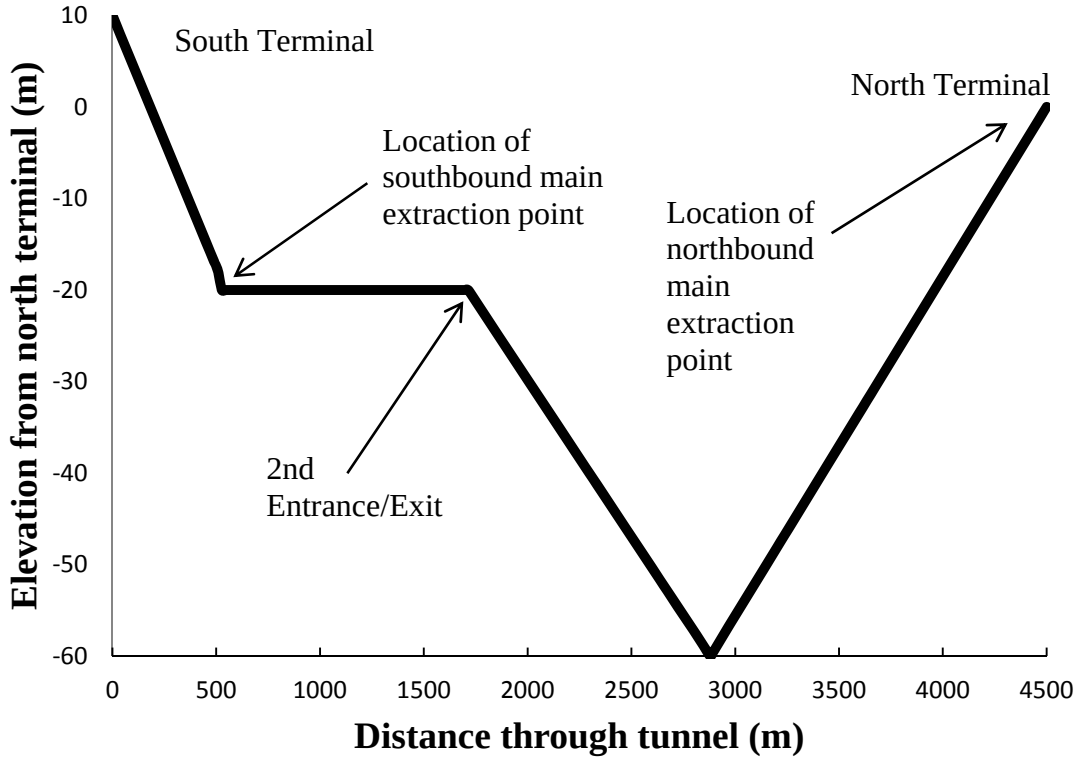

Figure 1: Schematic diagram of the tunnel.

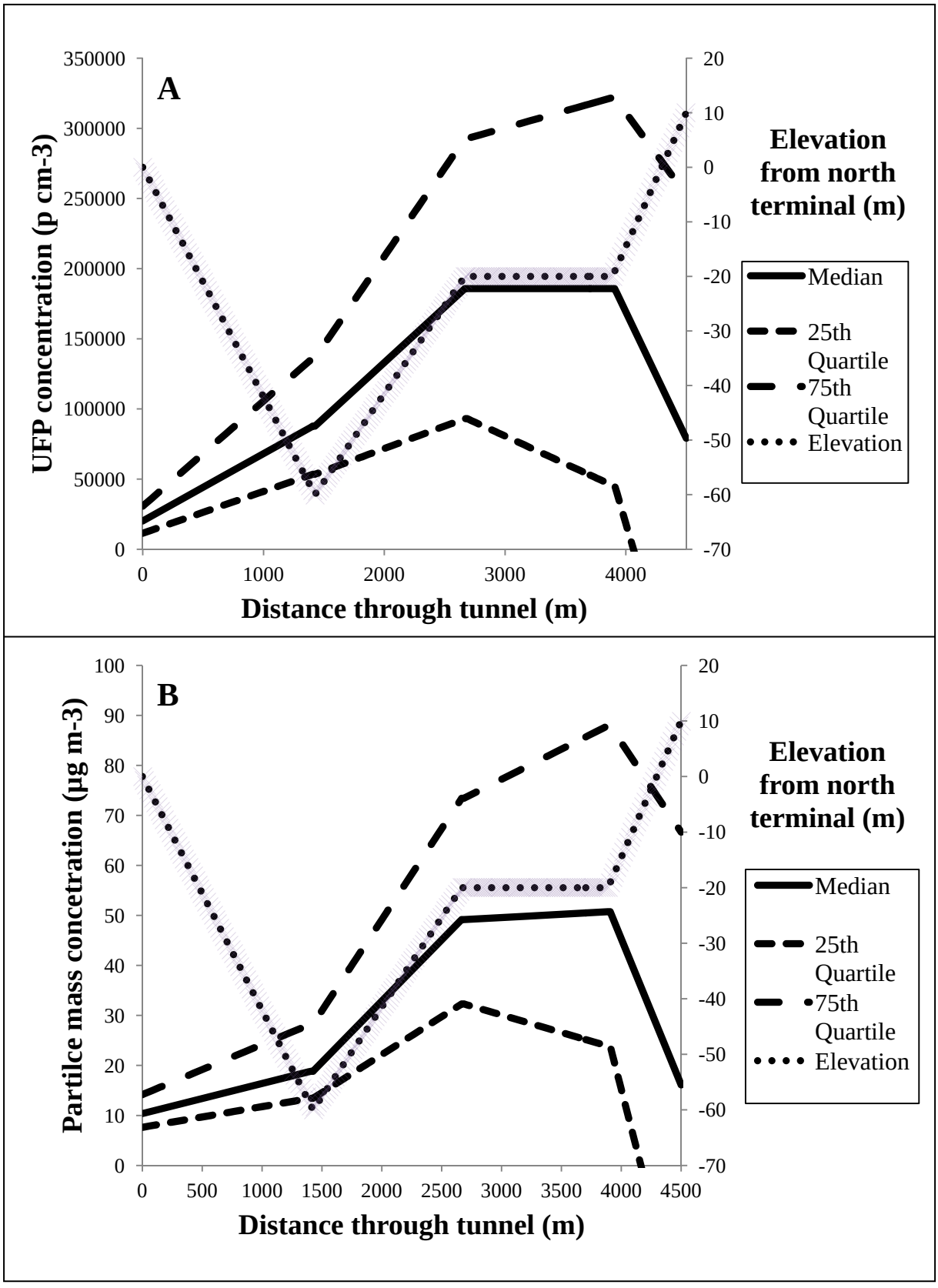

Figure 2: Particle number (A) and mass (B) concentration evolution by distance through the tunnel for all northbound tunnel runs

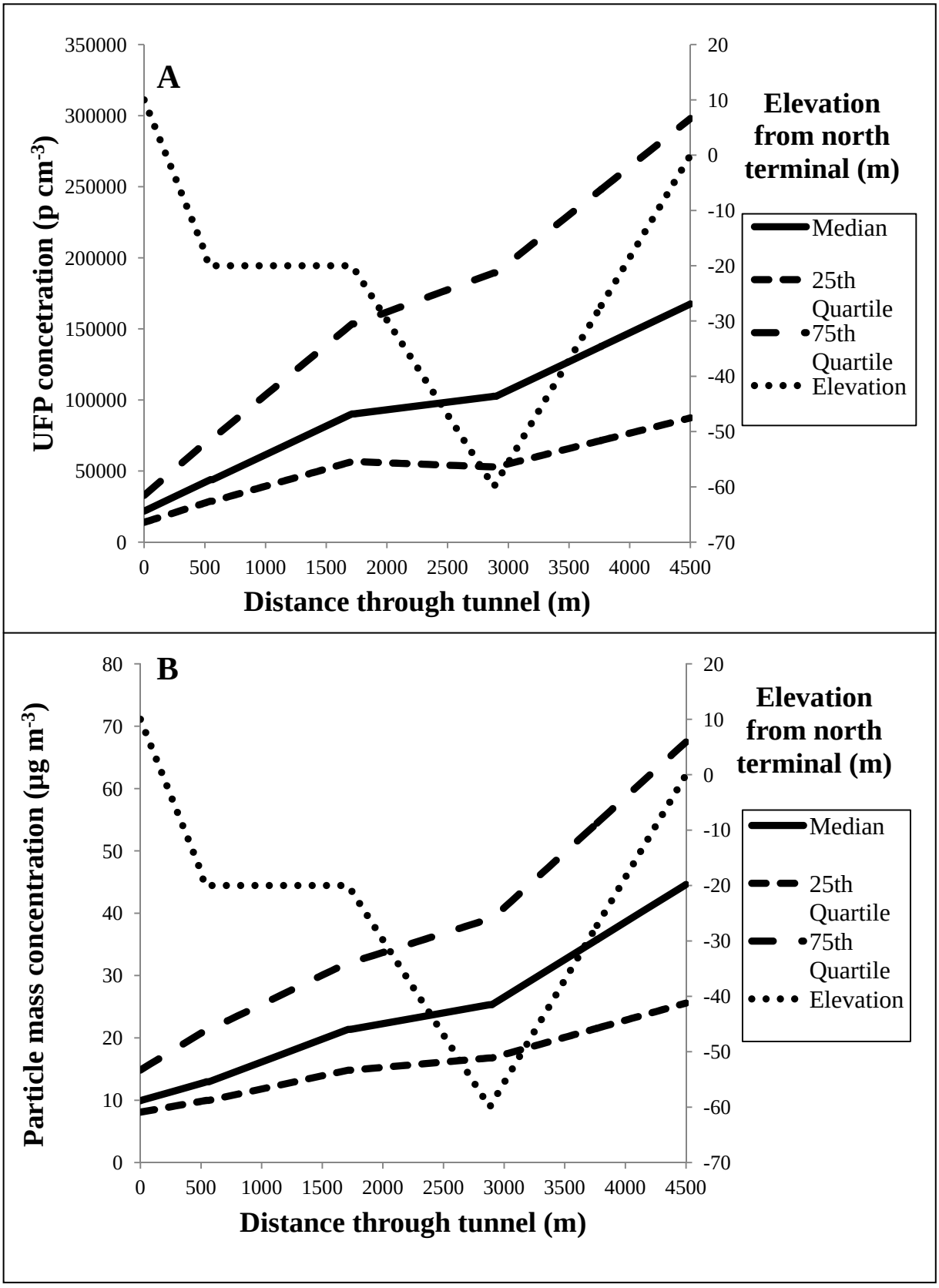

Figure 3: Particle number (A) and mass (B) concentration evolution by distance through the tunnel for all southbound runs.

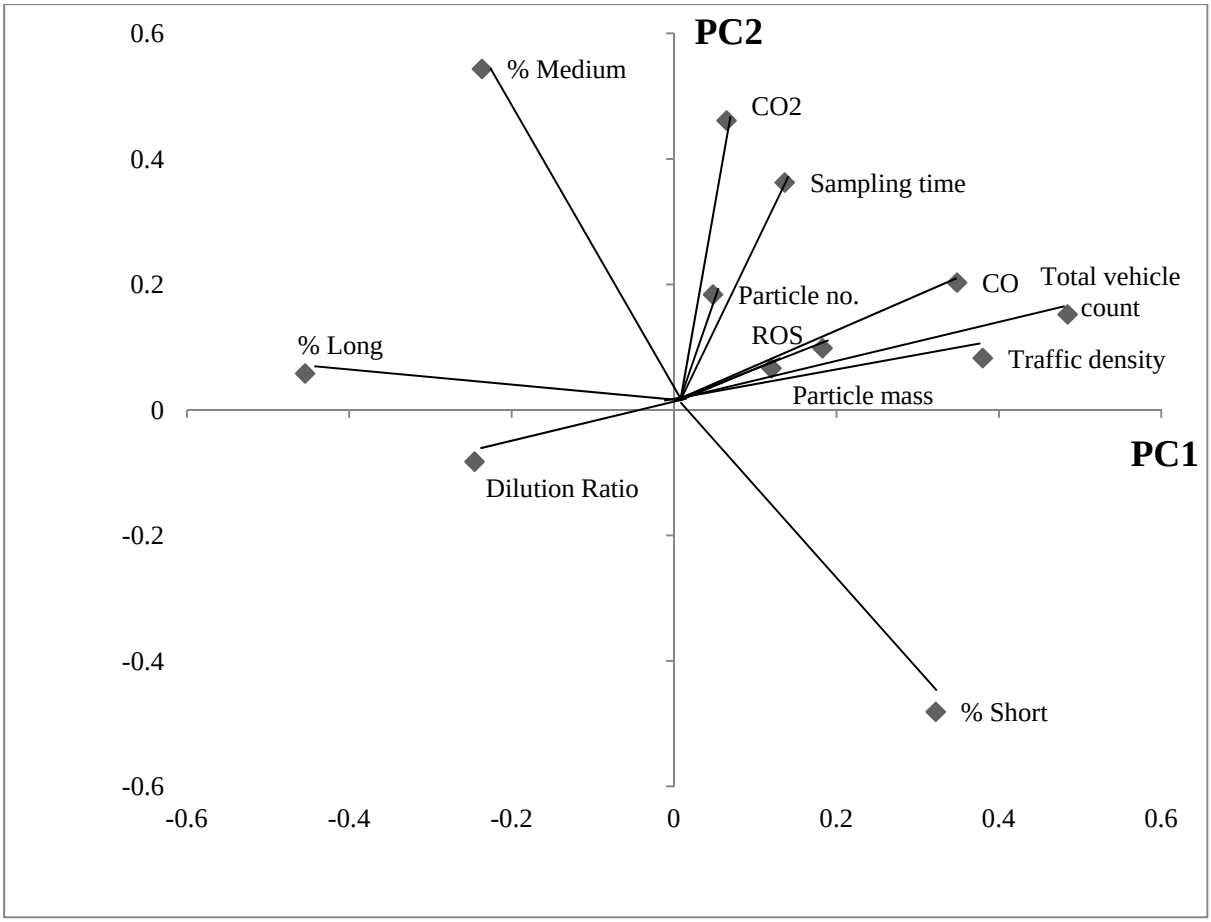

Figure 6: Loadings plot of the August/September campaign data

Campaign	*Temperature (°C)*	*Relative Humidity (%)*	*CO (ppm)*	*CO_2 (ppm)*	*Particle Number (p cm^{-3})*	*Particle Mass (µg m^{-3})*
I	29	61	6.4	536	$1.43x10^5$	36
II	22	50	[a]	484	$1.23x10^5$	26
III	24	54	4.9	665	$1.32x10^5$	36

Table 1: Average trip concentrations of the measured parameters during each campaign. [a]CO data was not collected during campaign II.

Date	Time	*ROS Concentration*		*Vehicle Count*	*Traffic Composition*	
		nmol mg^{-1}	nmol m^{-3}	Veh h^{-1}	% HDV	Dilution Ratio
23/08/2010	1000-1100	286	13	693	44	380
	1400-1500	295	12	848	29	861
1/09/2010	0700-0800	226	20	1362	15	431
	1100-1200	760	24	721	28	836
	1600-1700	1183	36	1515	25	453
10/09/2010	1200-1300	180	6	885	32	918
	1500-1600	159	6	1336	24	683
16/09/2010	0730-0830	385	8	1325	17	556
	1100-1200	212	5	774	28	856
	1600-1700	335	8	1564	23	480
23/09/2010	0900-1000	75	2	768	23	644
	1530-1630	213	6	1337	21	542
28/09/2010	1000-1100	0	0	733	25	494
	1600-1700	117	5	1444	38	a

Table 2: Particle associated ROS concentrations for each sample in the campaign III. Cells that are shaded represent peak traffic times in the tunnel. Traffic data is average of northbound and southbound bores. a There was an error with the CO_2 probe for this sample